

# Infrared Spectra of Pentachlorofluoroethane, 1, 2-Dichlorotetrafluoroethane, and 1-Bromo-2-Fluoroethane

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The infrared absorption spectra of pentachlorofluoroethane and 1,2-dichlorotetrafluoroethane have been measured from 2 to 40  $\mu$ . Several bands were found in the region from 25 to 40  $\mu$ , which had not been previously investigated. The spectrum of 1-bromo-2-fluoroethane has also been measured in the spectral region from 2 to 40  $\mu$ , and many bands were observed. A list of the observed bands and the frequency assignments for the three molecules are given.

In recent years much interest has been shown in the spectroscopy of fluorinated hydrocarbons. Glockler and Sage,<sup>2,3</sup> for example, have given the Raman spectra of such compounds and Smith, Nielsen, and coworkers<sup>4,5</sup> have given the infrared and Raman spectra of many fluorinated ethanes, along with frequency assignments for some of them. In this report we present spectra and assignments for three fluorinated hydrocarbons, pentachlorofluoroethane ( $\text{CCl}_3\text{CCl}_2\text{F}$ ), 1,2-dichlorotetrafluoroethane ( $\text{CClF}_2\text{CClF}_2$ ), and 1-bromo-2-fluoroethane ( $\text{CH}_2\text{BrCH}_2\text{F}$ ). The Raman spectrum of  $\text{CClF}_2\text{CClF}_2$  has been reported by Glockler and Sage (see footnote 2) and the infrared spectra of  $\text{CCl}_3\text{CCl}_2\text{F}$  and  $\text{CClF}_2\text{CClF}_2$  have been reported by Smith and Nielsen (see footnotes 4 and 5). We have extended the infrared spectra of the last two named molecules to 40  $\mu$  and present the spectrum of the third in the 2 to 40  $\mu$  range.

The spectra of these compounds were obtained on a Perkin-Elmer model 12C spectrometer. The prisms used in the various spectral ranges were: 1 to 5  $\mu$ , lithium fluoride; 2 to 16  $\mu$ , sodium chloride; 14 to 24  $\mu$ , potassium bromide; and 23 to 40  $\mu$ , thallium bromide-iodide.

Figure 1 shows the spectrum of  $\text{CCl}_3\text{CCl}_2\text{F}$ . It was obtained by comparing the absorption of the compound with the absorption of air. These observations were then reduced to the percent transmittance of the compound. Figures 2 and 3 present the spectra of  $\text{CClF}_2\text{CClF}_2$  and  $\text{CH}_2\text{BrCH}_2\text{F}$  obtained in a similar manner. These compounds were examined in various states and under various experimental conditions, the conditions being described on the figures and in the captions.

Because these molecules do not form a closely related series of substituted ethanes, it would not be expected that their spectra would show many similarities. A general feature of the three spectra is that most of the intense bands fall between 8 and 20  $\mu$ .

In tables 1 through 3 are given the observed infrared bands, the available Raman data, and these frequency assignments for the three molecules. These

assignments were made on the basis of analogy with the assignments of closely related structures which have previously been studied. Table 4 compares these assignments for  $\text{CH}_2\text{BrCH}_2\text{F}$  with the wave number ranges for the various vibrations of three molecules,  $(\text{CH}_2\text{Cl})_2$ ,  $(\text{CH}_2\text{Br})_2$ , and  $\text{CH}_2\text{BrCH}_2\text{Cl}$ . These values are taken from the assignments of J. U. Brown and W. S. Sheppard, who have kindly allowed the use of the results of their work, which now await publication. These four molecules listed in table 4 are expected to exist in two isomeric forms, *trans* and *gauche*. In this table are given the differences in going from the *gauche* to the *trans* form for individual vibrations. The assignments for  $\text{CCl}_3\text{CCl}_2\text{F}$  and  $\text{CClF}_2\text{CClF}_2$  were made in the same way by comparing their vibrations with related molecules.

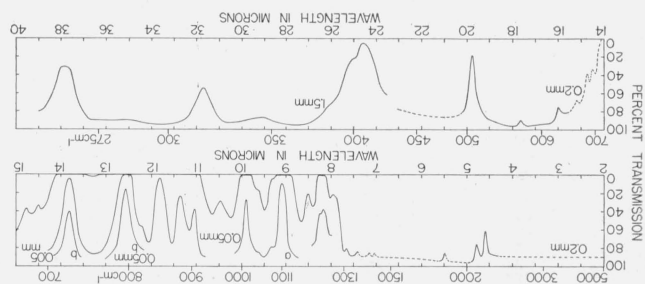


FIGURE 1. Infrared absorption spectrum of  $\text{CCl}_3\text{CCl}_2\text{F}$ .

The spectrum of this substance, a solid at room temperature, was obtained by making a saturated solution in  $\text{CS}_2$ . Insert A was obtained by mixing 1 part of the saturated solution with 4 parts of  $\text{CS}_2$ ; insert B was obtained by mixing 1 part of the saturated solution with 20 parts of  $\text{CS}_2$ . Dotted lines represent regions of intense atmospheric absorption and of absorption of the solvent.

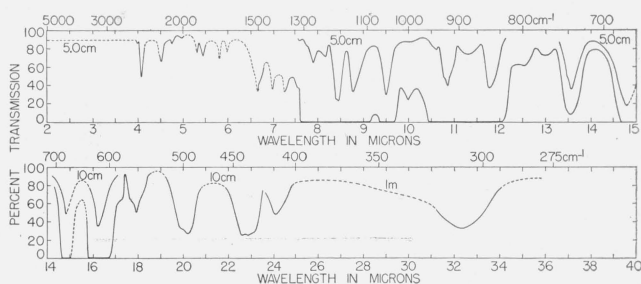


FIGURE 2. Infrared absorption spectrum of  $\text{CClF}_2\text{CClF}_2$ .

This spectrum is of the vapor state. The pressure was atmospheric, except for the inserts which were obtained by removing some of the vapor. The cell thickness employed for the different regions are marked on the figure. Dotted lines are used in regions of intense atmospheric absorption.

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<sup>2</sup> G. Glockler and C. Sage, J. Chem. Phys. **8**, 291 (1940).

<sup>3</sup> G. Glockler and C. Sage, J. Chem. Phys. **9**, 387 (1941).

<sup>4</sup> D. C. Smith, J. Reed Nielsen, L. H. Berryman, H. H. Claassen, and R. L. Hudson, NRL Report 3567.

<sup>5</sup> D. C. Smith, M. Alpert, R. A. Saunders, G. M. Brown, and N. B. Moran, NRL Report 3924.

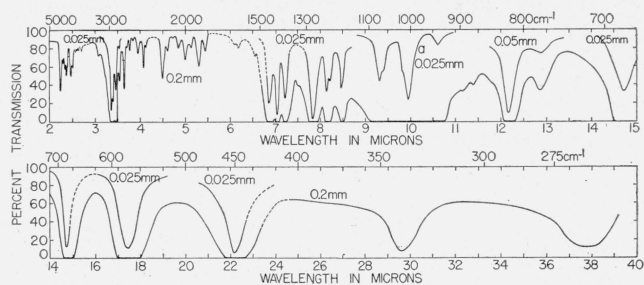


FIGURE 3. Infrared absorption spectrum  $\text{CH}_2\text{BrCH}_2\text{F}$ .

This spectrum is of the liquid state, except for insert A, which was obtained by diluting with  $\text{CS}_2$  in the ratio of 1:20.

TABLE 1. Observed infrared frequencies and band interpretations of  $\text{CCl}_3\text{CCl}_2\text{F}$

Two interpretations are presented, one assuming the existence of an unobserved band at  $170\text{ cm}^{-1}$ .

Frequency	Intensity	Interpretation	Interpretation by using a $170\text{ cm}^{-1}$ frequency
$\text{cm}^{-1}$			
264	m	C—Cl	
315	m	C—Cl	
400	s	Cl—C—F 904—506	
406	s	Cl—C—F	
506	s	C—C <sub>v</sub>	
567	vw	880—315	400+170 406+170
625	vw	$2 \times 315$	795—170
658	w	264+400	
677	w	264+406 ]	[ 506+170
689	w	1100—406 ]	[ 847—170
724	vs	C—Cl <sub>v</sub>	
795	vs	C—Cl <sub>v</sub>	
818	w	506+315 $2 \times 408$	
847	s	C—Cl <sub>v</sub>	
880	m	C—Cl <sub>v</sub>	
904	m	C—Cl <sub>v</sub>	
954	w	-----	795+170
1009	vs	$2 \times 506$	847+170
1041	w	724+315	884+170
1074	w	-----	904+170
1100	vs	C—F <sub>v</sub>	
1176	m	904+264	
1215	s	904+315	
1225	s	724+506	
1256	m	904+400 904+406	
1267	m	847+506	1100+170
1310	vw	904+506	
1350	vw	847+506	
1399	vw	904+506	
1418	vw	1100+315	
1825	w	1100+724	
2088	w	$2 \times 795+506$	
		$2 \times 847+400$	
		$724+847+506$	
2179	w	$3 \times 724$ $2 \times 1100$	
		$2 \times 880+400$	

TABLE 2. Observed infrared and Raman frequencies and interpretations of  $\text{CClF}_2\text{CClF}_2$ 

The Raman frequencies are those of Glockler and Sage (see footnote 2 of text)

Infrared frequency	Intensity	Raman frequency	Interpretation	
			<i>Trans</i>	<i>Gauche</i>
310	m	171.4	-----	C—Cl <sub>δ</sub>
		207.4	C—Cl <sub>δ</sub>	C—Cl <sub>δ</sub>
		253.1	C—Cl <sub>δ</sub>	
		309.5	-----	C—F <sub>2</sub> δ
		325.7	C—F <sub>2</sub>	
415 437 442.5	m s s	360.0	[ CF <sub>2</sub> <sub>r</sub> CF <sub>2</sub> <sub>w</sub> CF <sub>2</sub> <sub>r</sub> CF <sub>2</sub> <sub>w</sub>	
		399.9		
		-----		
		443.9		CF <sub>2</sub> δ
497 503	s s	497.7	-----	[ CF <sub>2</sub> <sub>r</sub> CF <sub>2</sub> <sub>w</sub>
		503.4	-----	
		542.8	CF <sub>2</sub> <sub>t</sub>	
559 583	m w	556.5	-----	[ CF <sub>2</sub> <sub>t</sub> 734—171 1053—498
		-----	CF <sub>2</sub> <sub>t</sub>	
		-----		
617 676	vs vs	-----	CF <sub>2</sub> δ	
		677.0	-----	C—C <sub>p</sub> C—Cl <sub>p</sub>
		699.7	C—Cl <sub>p</sub>	
736	vs	723.4	C—C <sub>p</sub>	
		734.1		
772 796 847 883 921	w w vs m vs	-----	415+360 437+325	[ 498+310 498+310
		-----	437+360	
		-----	C—Cl <sub>p</sub>	
		-----	1138—253	2×443 1053—171
		914.7	-----	CF <sub>p</sub>
942 1007 1051	w w vs	-----	617+325 360+583	498+444 503+444
		-----	-----	2×503
		1043.5	732+325 617+437	734+310
		1055.9	-----	CF <sub>p</sub>
1138	vs	1063.7	CF <sub>p</sub>	
		1111.6	700+415 847+253	677+444
		-----	CF <sub>p</sub>	
		1172.5	CF <sub>p</sub>	
1185 1192	vs	-----	CF <sub>p</sub>	
		-----		
		-----		
1227 1267 1316	m m w	-----	-----	CF <sub>p</sub>
		1269.6	-----	CF <sub>p</sub>
		-----	700+617	
1357 1435 1504	w w w	-----	-----	[ 1053+310 2×677 923+444 1268+171 1053+444
		-----	1188+253	
		-----	1188+325 1184+360	
		-----	[ 1064+437	-----
1675 1727	w w	-----	1064+417 1138+543	1227+444
		-----	1118+543	[ 1053+677 1227+495 1227+503
1842 1887 2110 2222 2459	w w vw w w	-----	1138+700	2×921
		-----	1188+700	
		-----	-----	2×1053
		-----	-----	2×1227

TABLE 3. Observed infrared frequencies and interpretations of CH<sub>2</sub>BrCH<sub>2</sub>F

Frequency	Intensity	Interpretation	
		<i>Trans</i>	<i>Gauche</i>
<i>cm<sup>-1</sup></i>			
264	m	C—X <sub>δ</sub>	
338	m	-----	C—X <sub>δ</sub>
451	s	-----	C—X <sub>δ</sub>
574	s	-----	C—Cl <sub>v</sub>
679	s	C—Cl <sub>v</sub>	
776	w	CH <sub>2</sub> <sub>r</sub> (rocking)	
822	s	-----	CH <sub>2</sub> <sub>r</sub>
847	w	-----	1182+338
879	vw	-----	
897	vw	-----	2×451
943	s	-----	CH <sub>2</sub> <sub>r</sub>
1006	vs	CH <sub>2</sub> <sub>r</sub>	C—F <sub>v</sub>
1020	m	-----	C—C <sub>v</sub>
1060	m	C—C <sub>v</sub>	
1075	s	C—F <sub>v</sub>	
1182	s	-----	CH <sub>2</sub> <sub>t</sub>
1218	w	CH <sub>2</sub> <sub>t</sub>	
1229	s	CH <sub>2</sub> <sub>w</sub>	
1279	vs	CH <sub>2</sub> <sub>t</sub>	CH <sub>2</sub> <sub>w</sub>
1333	w	CH <sub>2</sub> <sub>w</sub>	
1389	vs	-----	CH <sub>2</sub> <sub>w</sub>
1422	vs	-----	CH <sub>2</sub> <sub>δ</sub>
1461	s	CH <sub>2</sub> <sub>δ</sub>	
1529	vw	-----	1182+338
1618	w	-----	1279+338
1639	w	-----	1182+451 2×822
1845	w	1060+776 1075+776	1020+822 1006+943
1890	m	1218+679	1389+451 1279+574
1953	w	1279+679	2×943
2008	w	2×1006 1229+776	1389+574 943+1020
		1333+679	1182+822 2×1006
2066	w	1006+1060 1279+776	
2123	vw	2×1060	1182+943
2172	w	-----	1006+1182
2226	m	1006+1218 1006+1229	1279+943
2428	w	2×1218	1422+1006
2458	m	1461+1006 2×1229	1279+1182
2534	w	1461+1075	
2611	vw	1333+1279	1422+1182
2660	w	2×1333	1389+1279
2725	s	1461+1279	
2756	m	1333+1461	
2832	m	-----	2×1422
2894	s	2×1461	
2949	s	CH <sub>v</sub> 4 modes	CH <sub>v</sub> 4 modes
2976	s	-----	
3125	w	-----	
3246	w	2976+264	
3731	vw	2949+776	
3817	vw	-----	
3861	vw	-----	2949+822
3921	vw	-----	2976+943
4013	w	2949+1060	
4058	m	2976+1075	
4235	w	2949+1279	2949+1279
4290	m	2949+1333	
4329	w	-----	2949+1389
4354	m	-----	2976+1389

TABLE 4. Comparison of the frequencies below 1,500  $\text{cm}^{-1}$  of  $(\text{CH}_2\text{Cl})_2$ ,  $(\text{CH}_2\text{Br})_2$ , and  $\text{CH}_2\text{BrCH}_2\text{Cl}$ 

The values listed for X-Y are the range of values for these three compounds, those listed after Br-F are the values for  $\text{CH}_2\text{BrCH}_2\text{F}$ . Raman values are included where available. "Not observed" means no infrared values have been reported.

Frequencies below 1,500 $\text{cm}^{-1}$					
$\text{CH}_2$			$\text{CH}_2$ wag		
<i>Trans</i>	$A_g, A'$	$B_u, A'$	<i>Trans</i>	$A_g, A'$	$B_u, A'$
X-Y----- Br-F-----	1438 to 1448 1461	1439 to 1453 1461	X-Y----- Br-F-----	1250 to 1301 1333	1192 to 1231 1229
<i>Gauche</i>	$A, A$	$B, A$	<i>Gauche</i>	$A, A$	$B, A$
X-Y----- Br-F-----	1419 to 1433 1422	1419 to 1433 1422	X-Y----- Br-F-----	1278 to 1312 1389	1248 to 1283 1279
$\text{CH}_2$ twist			$\text{CH}_2$ rock		
<i>Trans</i>	$A_u, A''$	$B_g, A''$	<i>Trans</i>	$A_u, A''$	$B_g, A''$
X-Y----- Br-F-----	1095 to 1124 1218	1250 to 1265 1279	X-Y----- Br-F-----	745 to 773 776	933 to 992 1006
<i>Gauche</i>	$A, A$	$B, A$	<i>Gauche</i>	$A, A$	$B, A$
X-Y----- Br-F-----	Not observed Not observed	1105 to 1145 1182	X-Y----- Br-F-----	899 to 944 943	834 to 880 822
C—Halogen <sub>v</sub>			C—Halogen		
<i>Trans</i>	$A_g, A'$	$B_u, A'$	<i>Trans</i>	$A_g, A'$	$B_u, A'$
X-Y----- Br-F-----	657 to 750 1075	586 to 711 679	X-Y----- Br-F-----	190 to 302 264	Not observed. Not observed.
<i>Gauche</i>	$A, A$	$B, A$	<i>Gauche</i>	$A, A$	$B, A$
X-Y----- Br-F-----	551 to 665 1006	583 to 678 574	X-Y----- Br-F-----	272 to 327 338	355 to 412 451
C—C <sub>v</sub>			Torsion		
<i>Trans</i>	$A_g, A'$		<i>Trans</i>	$A_u, A'$	
X-Y----- Br-F-----	934 to 992 1006		X-Y----- Br-F-----	Not observed. Not observed.	
<i>Gauche</i>	$A, A$		<i>Gauche</i>	$A, A$	
X-Y----- Br-F-----	894 to 943 943		X-Y----- Br-F-----	Not observed. Not observed.	

WASHINGTON, January 5, 1953.